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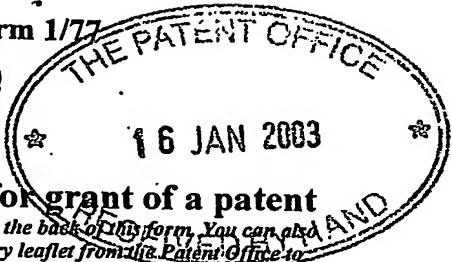
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P032909GB

2. Patent application number

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0301034.5

3. Full name, address and postcode of the or of each applicant *(underline all surnames)*

08544991001

Patents ADP number *(if you know it)*

DUPONT TEIJIN FILMS U.S. LIMITED PARTNERSHIP
BUILDING 27
BARLEY MILL PLAZA
ROUTES 141 & 48
WILMINGTON, DELAWARE 19805
USA

If the applicant is a corporate body, give the country/state of its incorporation

DELAWARE, USA

4. Title of the invention

POLYMERIC FILM AND COATING

5. Name of your agent *(if you have one)*

Carpmaels & Ransford

"Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*

43 Bloomsbury Square
London
WC1A 2RA

Patents ADP number *(if you know it)*

83001



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Country

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Number of earlier application

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11. I/We request the grant of a patent on the basis of this application.

Signature  Date 16th January 2003
Carpmaels & Ransford

12. Name and daytime telephone number of person to contact in the United Kingdom

Dr. B.R. Cockerton 020-7242 8692

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POLYMERIC FILM AND COATING

The present application is concerned with anti-microbial polymeric film, particularly polyester film.

5

The preparation of polymeric films having anti-microbial properties is well-known. Such films are of use in the provision of anti-microbial surfaces, for example in medical and catering environments. The anti-microbial properties are imparted using an anti-microbial agent. The preparation of such films typically involves disposing the anti-microbial agent 10 into the polymer matrix or on one or more surface(s) as a coating. Desirably, the anti-microbial agent should have a broad spectrum of activity over different microbes, and a low toxicity profile for higher organisms. Metal ions, particularly silver ions, have long been known to exhibit anti-fungal, anti-bacterial and anti-algal activity (hereinafter referred to as anti-microbial activity). Recently, it has been proposed to use an anti- 15 microbial metal ion supported on zirconium phosphate, as disclosed in, for instance, US-5441717, JP-A-3/83905 and US-5296238.

Anti-microbial agents are relatively expensive and the consumer must generally balance anti-microbial efficacy against cost. It would be desirable to provide more economical anti- 20 microbial films for a given anti-microbial efficacy, or films having greater anti-microbial efficacy for a given cost. In addition, existing anti-microbial films do not generally exhibit barrier properties to moisture and/or oxygen which are sufficient for packaging applications, for instance food packaging applications. In addition, existing anti-microbial films do not generally exhibit good optical properties, such as low haze and high gloss, 25 relative to a film without the anti-microbial agent. It is an object of this invention to provide an anti-microbial film which addresses one or more of the afore-mentioned problems.

According to the present invention, there is provided an anti-microbial polymeric film 30 comprising a polymeric substrate layer and a coating comprising an anti-microbial compound in an amount of from about 0.1 to about 5.0% by weight of the coating layer, wherein said coating has a thickness of from about 0.01 to about 14.0 μm .

The inventors have unexpectedly found that, for a given amount of anti-microbial agent, a relatively thinner coating provides greater anti-microbial activity than a thicker coating. Above a certain threshold of coating thickness, an increase in the amount of anti-microbial agent in the coating does not provide a proportional increase in anti-microbial efficacy.

- 5 Further, provided the thickness of the coating is kept below a certain threshold, the value of which may be correlated to the particle size of the anti-microbial agent, then a lower amount of anti-microbial agent having a relatively smaller particle size can be used without detriment to anti-microbial activity. Moreover, the reduction in the amount of anti-microbial agent used produces a corresponding reduction in the haze of the coated film.

10

As used herein, the term "anti-microbial" means microbicidal activity or microbe growth inhibition in a microbe population. In one embodiment, the microbe(s) is/are selected from the group consisting of *Aspergillus niger*, *Staphylococcus aureus* and *Escherichia coli*. In one embodiment, the term "anti-microbial" means a greater than 1 log reduction,

- 15 preferably a greater than 2 log reduction, preferably a greater than 3 log reduction, and more preferably a greater than 4 log reduction in the growth of a population of microbes relative to a control.

- The anti-microbial agents include but are not limited to phthalimides, acetamides, 20 phthalonitriles, benzoic acid and its derivatives including hydroxy benzoates, isothiazolinones, nitropropane diols, carbamates, methyl ureas, benzimidazoles, salicylanilides, triclosan-based anti-microbial agents, benomy, sorbic acid and its derivatives, chitin and chitosan and their derivatives, chlorine dioxide-generating powder systems, mercury acetates, organozinc compounds, metals such as silver, copper and zinc, 25 and ions of such metals.

Liquid anti-microbial agents include dibromocyanoacetamide (for example, Amerstat.RTM. 300 made by Drew Industrial Division of Ashland Chemicals, Boonton, N.J., USA). Solid anti-microbial agents include 2-bromo-2-nitropropane-1,3-diol (for 30 example, Canguard RTM 409 made by Angus Chemical Co., Buffalo Grove, Illinois, USA) and 3,5-dimethyltetrahydro-1,3,5-2H-thiazine-2-thione (for example, Nuosept RTMS made by Creanova, Inc., Piscataway, N.J., USA or Troysan RTM 142 made by Troy Chemical Corp., West Hanover, N.J., USA). Other solid anti-microbial agents include

- N- (trichloromethyl)-thiophthalimide (for example, Fungitrol RTM 11 made by Creanova, Inc.), butyl-p-hydroxy-benzoate (for example, Butyl Parabens RTM made by International Sourcing Inc., Upper Saddle River, N.J., USA), diiodomethyl-p-tolysulfone (for example, Amical RTM WP made by Angus Chemical Co.), and tetrachloroisophthalonitrile (for 5 example, Nuocide RTM 960 made by Creanova, Inc.).

- With regard to metal-containing anti-microbial agents, silver-containing agents are particularly preferred. Sources of silver for anti-microbial use include metallic silver, silver salts and organic compounds that contain silver. Silver salts include silver carbonate, silver 10 sulfate, silver nitrate, silver acetate, silver benzoate, silver chloride, silver fluoride, silver iodate, silver iodide, silver lactate, silver nitrate, silver oxide and silver phosphates. Organic compounds containing silver may include for example, silver acetylacetone, silver neodecanoate and silver ethylenediaminetetraacetates.
- 15 Silver containing zeolites (for example, AJ10D containing 2.5% silver as Ag(I), made by AgION.TM. Tech. L.L.C., Wakefield, Mass., USA) are of particular use. Zeolites are useful because when carried in a polymer matrix they may provide silver ions at a rate and concentration that is effective at killing and inhibiting microorganisms without harming higher organisms.

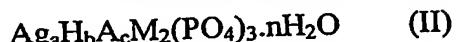
- 20 In a preferred embodiment, the anti-microbial compound is selected from those disclosed in US-5441717 or US-5296238. Preferably, the anti-microbial compound has formula (I):



wherein

- 25 M^1 is at least one metal ion selected from silver, copper, zinc, tin, mercury, lead, iron, cobalt, nickel, manganese, arsenic, antimony, bismuth, barium, cadmium and chromium; A is at least one ion selected from an alkali or alkaline earth metal ion; M^2 is a tetravalent metal ion; a and b are positive numbers and c is 0 or a positive number such that $(ka + b + mc) = 1$;
- 30 k is the valence of metal M^1 ;
- m is the valence of metal A ; and
- $0 \leq n \leq 6$.

Preferably, M¹ is silver and the anti-microbial compound has formula (II):



wherein

A is at least one ion selected from an alkali or alkaline earth metal ion;

5 M is a tetravalent metal ion;

a, b and c are positive numbers such that (a + b + mc) = 1;

m is the valence of metal A; and

0 ≤ n ≤ 6.

10 The anti-microbial compounds of formula (I) may be prepared according to the methods described in US-5441717 or US-5296238. The anti-microbial silver ion is supported on the zirconium phosphate. The metal A is preferably selected from lithium, sodium, potassium, magnesium and calcium, and is preferably sodium. The metal M is preferably selected from zirconium, titanium and tin, preferably from zirconium and titanium, and is

15 preferably zirconium.

The value of the parameter "a" is preferably at least 0.001, more preferably at least 0.01, and is preferably in the range of 0.01 to 0.5, more preferably 0.1 to 0.5, more preferably 0.10 to 0.30. In one embodiment, the value of the parameter "a" is in the range from 0.4 to

20 0.5 or in the range 0.15 to 0.25, preferably in the range 0.4 to 0.5.

The value of the parameter "b" is preferably at least 0.2, more preferably in the range of 0.2 to 0.7, more preferably in the range of 0.2 to 0.60. In one embodiment, the value of the parameter "b" is on the range 0.2 to 0.3.

25

In one embodiment, the antimicrobial compound is selected from Ag_{0.18}Na_{0.57}H_{0.25}Zr₂(PO₄)₃ and Ag_{0.46}Na_{0.29}H_{0.25}Zr₂(PO₄)₃.

30 The polymeric substrate layer is a self-supporting film or sheet by which is meant a film or sheet capable of independent existence in the absence of a supporting base. The substrate may be formed from any suitable film-forming polymer, including polyolefin (such as polyethylene and polypropylene), polyamide (including nylon), PVC and polyester. The polymeric substrate may be oriented, such as oriented polypropylene or polyethylene

terephthalate (PET), or amorphous, as discussed in more detail below. In a preferred embodiment, the substrate is polyester, and particularly a synthetic linear polyester.

- The preferred synthetic linear polyesters of the substrate may be obtained by condensing
- 5 one or more dicarboxylic acids or their lower alkyl (up to 6 carbon atoms) diesters, eg terephthalic acid, isophthalic acid, phthalic acid, 2,5-, 2,6- or 2,7-naphthalenedicarboxylic acid, succinic acid, sebacic acid, adipic acid, azelaic acid, 4,4'-diphenyldicarboxylic acid, hexahydro-terephthalic acid or 1,2-bis-p-carboxyphenoxyethane (optionally with a monocarboxylic acid, such as pivalic acid) with one or more glycols, particularly an
- 10 aliphatic or cycloaliphatic glycol, e.g. ethylene glycol, 1,3-propanediol, 1,4-butanediol, neopentyl glycol and 1,4-cyclohexanedimethanol. An aromatic dicarboxylic acid is preferred. An aliphatic glycol is preferred. Polyesters or copolyesters containing units derived from hydroxycarboxylic acid monomers, such as ω -hydroxyalkanoic acids (typically C₃-C₁₂) such as hydroxypropionic acid, hydroxybutyric acid, p-hydroxybenzoic
- 15 acid, m-hydroxybenzoic acid, or 2-hydroxynaphthalene-6-carboxylic acid, may also be used.

In a preferred embodiment, the polyester is selected from polyethylene terephthalate and polyethylene naphthalate. Polyethylene terephthalate (PET) is particularly preferred.

- 20 The substrate may comprise one or more discrete layers of the above film-forming materials. The polymeric materials of the respective layers may be the same or different. For instance, the substrate may comprise one, two, three, four or five or more layers and typical multi-layer structures may be of the AB, ABA, ABC, ABAB, ABABA or ABCBA type. Preferably, the substrate comprises only one layer.

- In one embodiment, the substrate is a bilayer substrate wherein one layer (i.e. the layer remote from the surface coated with the anti-microbial composition) is a heat-sealable layer. Heat-sealable layers are well-known in the art and include polymeric materials such
- 30 as polyester, EVA or modified polyethylene. In one embodiment, the heat-sealable layer comprises a linear polyester resin, particularly a copolyester resin derived from one or more of the dicarboxylic acid(s) with one or more of the glycol(s) noted above.

Formation of the substrate may be effected by conventional techniques well-known in the art. Conveniently, formation of the substrate is effected by extrusion, in accordance with the procedure described below. In general terms the process comprises the steps of extruding a layer of molten polymer, quenching the extrudate and orienting the quenched 5 extrudate in at least one direction.

The substrate may be uniaxially-oriented, but is preferably biaxially-oriented, as noted above. Orientation may be effected by any process known in the art for producing an oriented film, for example a tubular or flat film process. Biaxial orientation is effected by 10 drawing in two mutually perpendicular directions in the plane of the film to achieve a satisfactory combination of mechanical and physical properties.

In a tubular process, simultaneous biaxial orientation may be effected by extruding a thermoplastics polymer tube which is subsequently quenched, reheated and then expanded 15 by internal gas pressure to induce transverse orientation, and withdrawn at a rate which will induce longitudinal orientation.

In the preferred flat film process, the substrate-forming polymer is extruded through a slot die and rapidly quenched upon a chilled casting drum to ensure that the polymer is 20 quenched to the amorphous state. Orientation is then effected by stretching the quenched extrudate in at least one direction at a temperature above the glass transition temperature of the polyester. Sequential orientation may be effected by stretching a flat, quenched extrudate firstly in one direction, usually the longitudinal direction, i.e. the forward direction through the film stretching machine, and then in the transverse direction. 25 Forward stretching of the extrudate is conveniently effected over a set of rotating rolls or between two pairs of nip rolls, transverse stretching then being effected in a stenter apparatus. Alternatively, the cast film may be stretched simultaneously in both the forward and transverse directions in a biaxial stenter. Stretching is effected to an extent determined by the nature of the polymer, for example polyethylene terephthalate is usually stretched so 30 that the dimension of the oriented film is from 2 to 5, more preferably 2.5 to 4.5 times its original dimension in the or each direction of stretching. Typically, stretching is effected at temperatures in the range of 70 to 125°C. Greater draw ratios (for example, up to about 8 times) may be used if orientation in only one direction is required. It is not necessary to

stretch equally in the machine and transverse directions although this is preferred if balanced properties are desired.

A stretched film may be, and preferably is, dimensionally stabilised under dimensional restraint at a temperature above the glass transition temperature of the polyester but below the melting temperature thereof, to induce crystallisation of the polyester. The actual heat-set temperature and time will vary depending on the composition of the film but should not be selected so as to substantially degrade the mechanical properties of the film. Within these constraints, a heat-set temperature of about 10 135° to 250°C is generally desirable, as described in GB-A-838708.

Where the substrate comprises more than one layer, preparation of the substrate is conveniently effected by coextrusion, either by simultaneous coextrusion of the respective film-forming layers through independent orifices of a multi-orifice die, and thereafter 15 uniting the still molten layers, or, preferably, by single-channel coextrusion in which molten streams of the respective polymers are first united within a channel leading to a die manifold, and thereafter extruded together from the die orifice under conditions of streamline flow without intermixing thereby to produce a multi-layer polymeric film, which may be oriented and heat-set as hereinbefore described. Formation of a multi-layer 20 substrate may also be effected by conventional lamination techniques, for example by laminating together a preformed first layer and a preformed second layer, or by casting, for example, the first layer onto a preformed second layer. Where the substrate comprises a heat-sealable layer, the heat-sealable layer may also be applied by conventional coating techniques.

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The substrate layer is suitably of a thickness between about 5 and 350µm, preferably from 12 to about 250 µm and particularly from about 20 to about 75 µm.

The coating composition in which the anti-microbial compound is contained may comprise 30 any suitable polymeric resin, including epoxy resins, polyester resins, acrylic resins, urethane resins and siloxanes.

- In a preferred embodiment, the coating comprising the anti-microbial agent is one which is sufficient to provide a barrier to oxygen and water. In one embodiment, the coating is sufficient to provide a water vapour transmission rate in the range of 0.01 to 10g/100 inches²/day, preferably 0.1 to 1.0g/100 inches²/day, and/or an oxygen transmission rate in the range of 0.01 to 10 cm³/100 inches²/day/atm, preferably 0.1 to 1 cm³/100 inches²/day/atm. Thus, the anti-microbial agent may be incorporated into conventional barrier coatings such as PVDC, PCTFE, PE, PP, EVOH or PVOH. PVDC layers are particularly suitable for providing a barrier to both gas and water vapour; EVOH and PVOH layers are particularly suitable for providing a barrier to gas; while PCTFE, PE and PP layers are particularly suitable for providing a barrier to water vapour. Suitable layers are known in the art and are disclosed, for instance, in US-5328724 (EVOH), US-5151331 (PVDC), US-3959526 (PVDC), US-6004660 (PVDC and PVOH). Suitable coat weights are in the range of 0.01 to 14 g/m², preferably 0.02 to 1.5 g/m².

-
- 15 In a further preferred embodiment, the coating comprising the anti-microbial agent is a sealant coating sufficient to provide a heat-seal strength of from 100 g/in to 2500 g/in when heat-sealed to itself according to the test method described herein.

- Thus, the anti-microbial agent may be incorporated into conventional heat-sealable or sealant coatings such as EVA, APET, PE or caprolactone. Suitable layers are well-known in the art. For instance, US-4375494 and US-6004660 describe amorphous copolyester sealant layers. Suitable coat weights are in the range of 0.5 to 14 g/m², preferably 1.0 to 10 g/m².

- 25 In a further embodiment, the coating comprising the anti-microbial agent provides both barrier and heat-seal properties, and PVDC coatings are suitable in this regard.

- In an alternative embodiment, a heat-sealable coating may be applied to one surface of the substrate, and a barrier layer on the other surface of the substrate. Anti-microbial agents may be incorporated into either or both layers in this embodiment.

The antimicrobial agent may be added to the coating composition in accordance with conventional procedures. For instance, the anti-microbial agent can be added directly to

the coating vehicle under adequate agitation, or it can be pre-dispersed or pre-mixed in an appropriate liquid medium (such as water or organic solvents). In an aqueous coating composition, surface emulsifiers may be used to help the dispersion of the anti-microbial agent. The pre-dispersed/pre-mixed anti-microbial agent is added to the main coating
5 composition under adequate agitation to ensure uniform distribution.

The anti-microbial compound is preferably present in an amount of from 0.2 to about 3.0%, and more preferably 0.5 to 2.0% by weight of the coating layer. In one embodiment, the anti-microbial compound is present at no more than 2.0% by weight of the coating
10 layer.

The coating may be applied to the substrate either in-line or off-line. The coating may be applied to an already-oriented substrate. However, application of the coating composition is preferably effected before or during the stretching operation(s). For instance, the coating
15 may be applied to the film substrate between the two stages (longitudinal and transverse) of a biaxial stretching operation. Thus, the film substrate may be stretched firstly in the longitudinal direction over a series of rotating rollers, coated with the coating composition, and then stretched transversely in a stenter oven, and preferably then heat-set. The coating composition may be applied to the polymer film substrate in aqueous or organic solution,
20 in a dispersion or in an emulsion by any suitable conventional coating technique such a gravure roll coating, reverse roll coating, dip coating, bead coating, slot coating or electrostatic spray coating.

Prior to deposition of the coating composition onto the substrate, the exposed surface
25 thereof may, if desired, be subjected to a chemical or physical surface-modifying treatment, as are well-known in the art, in order to improve the bond between that surface and the subsequently applied coating. Physical surface-modifying treatments include flame treatment, ion bombardment, electron beam treatment, ultra-violet light treatment and corona discharge.

30

The coating layer has a thickness in the range of about 0.01 to 14.0 μm . In one embodiment, the coating thickness is no more than about 5 μm , preferably no more than about 2 μm , and preferably in the range of about 0.02 to about 1.5 μm .

The present invention is particularly concerned with particulate anti-microbial agents and the inventors have found that the thickness of the coating layer may be correlated to the particle size of the anti-microbial compound. Thus, in a preferred embodiment, the 5 thickness (in μm) of the coating layer is in the range of 70 to 130%, preferably in the range 80 to 120%, more preferably in the range 90 to 110%, and more preferably in the range 95 to 105% of the volume distributed mean particle diameter (in μm) of the anti-microbial particles. In one embodiment, the thickness of the coating layer is less than the volume distributed mean particle diameter of the anti-microbial particles, preferably such that 10 thickness is in the range of 70 to 99 %, preferably in the range of 80 to 99%, more preferably in the range of 90 to 99% of the volume distributed mean particle diameter of the anti-microbial particles.

In a preferred embodiment, the particle size of the anti-microbial compound is such that
15 the volume distributed mean particle diameter is in the range of 0.4 to 10 μm , preferably 1.0 to 6.0 μm , and more preferably 1.0 to 3.0 μm .

The polymeric substrate may conveniently contain any of the additives conventionally employed in the manufacture of polymeric films. Thus, agents such as dyes, pigments, 20 voiding agents, lubricants, anti-oxidants, radical scavengers, UV absorbers, fire retardants, thermal stabilisers, anti-blocking agents, surface active agents, slip aids, optical brighteners, gloss improvers, prodegradents, viscosity modifiers and dispersion stabilisers may be incorporated in the substrate as appropriate. In particular the substrate may comprise a particulate filler. The filler may, for example, be a particulate inorganic filler 25 or an incompatible resin filler or a mixture of two or more such fillers. Particulate inorganic fillers include metal or metalloid oxides, such as alumina, silica (especially precipitated or diatomaceous silica and silica gels) and titania, calcined china clay and alkaline metal salts, such as the carbonates and sulphates of calcium and barium.

30 The inorganic filler, if used, should be finely-divided, and the volume distributed median particle diameter (equivalent spherical diameter corresponding to 50% of the volume of all the particles, read on the cumulative distribution curve relating volume % to the diameter of the particles - often referred to as the "D(v,0.5)" value) thereof is preferably in the range

from 0.01 to 5 μm , more preferably 0.05 to 1.5 μm , and particularly 0.15 to 1.2 μm . The size distribution of inorganic filler particles is also an important parameter. It is preferred that 99.9% by number of the inorganic filler particles should not exceed 30 μm , preferably should not exceed 20 μm , and more preferably should not exceed 15 μm . Preferably at least 90%, more preferably at least 95% by volume of the inorganic filler particles are within the range of the volume distributed median particle diameter \pm 0.8 μm , and particularly \pm 0.5 μm . Particle size of the filler particles may be measured by electron microscope, coulter counter, sedimentation analysis and static or dynamic light scattering. Techniques based on laser light diffraction are preferred. The median particle size may be determined by plotting a cumulative distribution curve representing the percentage of particle volume below chosen particle sizes and measuring the 50th percentile.

If employed in a coating layer, the filler particles, such as AerosilTM OX50 or SeahostarTM KEP30 or KEP50, may be present in an amount of from about 0 to about 5%, and more preferably 0.1 to 2.5% by weight relative to the weight of the polymer of the coating layer.

The components of the composition of a layer may be mixed together in a conventional manner. For example, by mixing with the monomeric reactants from which the layer polymer is derived, or the components may be mixed with the polymer by tumble or dry blending or by compounding in an extruder, followed by cooling and, usually, comminution into granules or chips. Masterbatching technology may also be employed.

The film preferably has a % of scattered visible light (haze) of <15%, preferably <12%, preferably <9%, preferably <6%, more preferably <3.5 % and particularly <2%, measured according to the standard ASTM D 1003. In this embodiment, the substrate layer is unfilled or filler is typically present in only small amounts, generally not exceeding 0.5% and preferably less than 0.2% by weight of the substrate polymer.

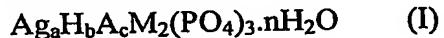
The 60° gloss value of the film (measured as described herein) is preferably at least 70, more preferably at least 80, and more preferably at least 85.

In a first preferred embodiment of the present invention, there is provided an anti-microbial polymeric film comprising a polymeric substrate layer and a coating comprising an anti-

microbial compound in an amount of from about 0.1 to about 5.0% by weight of the coating layer, wherein said coating has a thickness of from about 0.01 to about 14.0 μm , and wherein said coating is sufficient to provide a water vapour transmission rate in the range of 0.01 to 10g/100 inches²/day, and/or an oxygen transmission rate in the range of 5 0.01 to 10 cm³/100 inches²/day/atm.

In a second preferred embodiment of the present invention, there is provided an anti-microbial polymeric film comprising a polymeric substrate layer and a coating comprising an anti-microbial compound in an amount of from about 0.1 to about 5.0% by weight of 10 the coating layer, wherein said coating has a thickness of from about 0.01 to about 14.0 μm , and wherein said coating is sufficient to provide a heat-seal strength of the film to itself as measured herein of from 100 g/in to 2500 g/in.

~~In a third preferred embodiment of the present invention, there is provided an anti-~~
15 microbial polymeric film comprising a polymeric substrate layer and a coating comprising an anti-microbial compound in an amount of from about 0.1 to about 5.0% by weight of the coating layer, wherein said coating has a thickness of from about 0.01 to about 14.0 μm , and wherein said anti-microbial compound has formula (I):



20 wherein

A is at least one ion selected from an alkali or alkaline earth metal ion;

M is a tetravalent metal ion;

a, b and c are positive numbers such that $(a + b + mc) = 1$;

m is the valence of metal A; and

25 $0 \leq n \leq 6$.

The films obtainable using the invention may be used to provide an anti-microbial surface in a variety of applications, such as in medical and catering environments and equipment, and in food packaging. Other applications include restrooms, garbage disposals, animal 30 feed troughs, schools, swimming pool areas, automobile fixtures, public access fixtures, public seating, public transportation fixtures, toys, and other industrial, agricultural, commercial or consumer products.

The following test methods may be used to determine certain properties of the polymeric film:

- (i) Haze (% of scattered transmitted visible light) is measured using a Gardner Hazegard System XL-211, according to ASTM D 1003.
- 5 (ii) 60° gloss value of the film surface is measured using a Dr Lange Reflectometer REFO 3 (obtained from Dr Bruno Lange, GmbH, Dusseldorf, Germany) according to DIN 67530. Reflection was measured at three angles (20°, 60° and 85°) and measurements were carried out in both the machine and transverse directions of the film.
- 10 (iii) Water vapour transmission rate is measured according to ASTM D3985.
- (iv) Oxygen transmission rate is measured according to ASTM F1249.
- (v) Anti-microbial efficacy against bacteria was assessed using the "plate contact method" against 0.4 ml of 10^5 cells/ml in Na/K phosphate buffer with 22 hours exposure. Film samples were tested against *Staphylococcus aureus* and *Escherichia coli*.
- 15 (vi) Anti-microbial efficacy against fungi was assessed using a method based on ISO-846 using *Aspergillus niger* ATTC 6275. Each sample was inoculated with 0.1ml of a solution of 10^5 fungal spores per ml, and incubated at 29°C for up to 35 days. The fungal growth was assess by visual observation of the samples for samples where fungal growth that has localised to droplets. Efficacy is then rated in three categories:
- 20

Observed growth in droplets	Category
Droplets have dark growth; many spores	A
Droplets have light growth; few/no spores	B
Droplets have no or scarce growth	C

The rating of a given sample is then the number of droplets in each category.

- 25 (vii) Heat-seal strength is measured by heat-sealing a film sample to itself (coating layer contacted with coating layer) at 250°F under 30 psi with 0.35 seconds dwell time in a Sentinel® apparatus.

The invention is further illustrated by the following examples. It will be appreciated that the examples are for illustrative purposes only and are not intended to limit the invention as described above. Modification of detail may be made without departing from the scope of the invention.

5

EXAMPLES

In the following Examples the coating compositions were coated onto a biaxially oriented and heat-set polyethylene terephthalate film (Mylar® LBF Film, DuPont Teijin Films).

10

Examples 1 to 4

The coating composition was made by compounding the anti-microbial agent Alphasan™ RC2000 (Milliken) in a PVDC (Saran F278; Dow Chemicals) barrier coating. The coating composition was made according to conventional techniques as described herein and had

15 the following components:

Saran F278: 97.5% (Ex. 1), 97.0% (Ex. 2), 96.0% (Ex. 3), 98% (Ex. 4)

Alphasan RC2000: 0.5% (Ex. 1), 1.0 (Ex. 2), 2.0% (Ex. 3), 0.0% (Ex. 4)

Filler, 1.2% (Microtalc; Ashland Chemical Co. USA)

Acid Scavengers, 0.4% (Drapex 6.8; Crompton Corp. USA)

20 Wax 0.4% (Carnauba Wax; Frank B Ross Company USA)

THF and toluene are used as solvents and to make the bath at 20.0% solids.

The anti-microbial particles had a volume distributed mean particle diameter of 1.624 µm, and a size distribution such that 95% of the particles had a diameter of less than 4.697 µm. Example 4 is a comparative example. The coating composition is applied by roll coater

25 and dried in an oven at 120°C.

Examples 5 to 8

The coating composition was made by compounding the afore-mentioned anti-microbial agent Alphasan™ RC2000 (Milliken) in an APET (MOR-ESTER 49002; Rohm & Haas)

30 sealant coating. Example 8 is a comparative example. The coating composition was made according to conventional techniques as described herein and had the following components:

Mor-Ester 49002: 95.5% (Ex. 5-7), 97.5% (Ex. 8)

Alphasan RC2000: 2.0% (Ex. 5-7), 0.0% (Example 8)

Silica, 1.5% (Sylloid® 244; W. R. Grace & Co. USA)

Blocking agent, 1.0% (Kemamide E; Witco Chemical USA)

THF is used as the solvent and to make the bath at 16.0% solid.

- 5 The coating is applied by roll coater and dried in an oven at 100°C.

The physical properties of the films produced are given in Table 1. The coated films were analysed using the anti-microbial tests described herein. The results of the anti-bacterial tests are given in Figure 1. The error bars on the graph represent the standard deviation of
10 the data from two separate experiments.

Table 1

Example	Coat Thickness (μm)	RC2000 content (%) in the coating	ppb/cm ²	Amount Ag on coat surface ($\mu\text{g}/\text{cm}^2$)
1	1.0	0.5	1.166	0.0184
2	1.0	1.0	3.301	0.0521
3	1.0	2.0	7.470	0.1180
4	1.0	0.0	0	0
5	1.5	2.0	4.186	0.0661
6	3.0	2.0	2.029	0.0320
7	4.6	2.0	2.138	0.0338
8	1.5	0.0	0	0

- 15 Examples 1 to 3 show that when the coat thickness is kept low, the amount of silver available on the coated film surface is proportional to the amount of anti-microbial agent in the coating. A comparison of Examples 3, 5, 6 and 7 show that, for the same amount of anti-microbial agent in the coating, the amount of silver available on the surface decreases as the coat thickness increases.

20

Figure 1 shows that all of Examples 1 to 3 and 5 to 7 show anti-microbial efficacy.

Examples 2 to 8 were also tested in the anti-fungal assay described above and the results are shown in Table 2. After 14 days incubation, fungal growth on Examples 2, 3 and 5 was completely inhibited, and partially inhibited on Examples 6 and 7. No inhibition was observed for Example 4. A small degree of inhibition was also shown on Example 8.

5

Table 2 Antifungal Properties

Example	No. of Droplets in Category		
	A	B	C
2	0	0	10
3	0	0	10
4	10	0	0
5	0	0	10
6	0	3	7
7	0	8	2
8	6	4	0

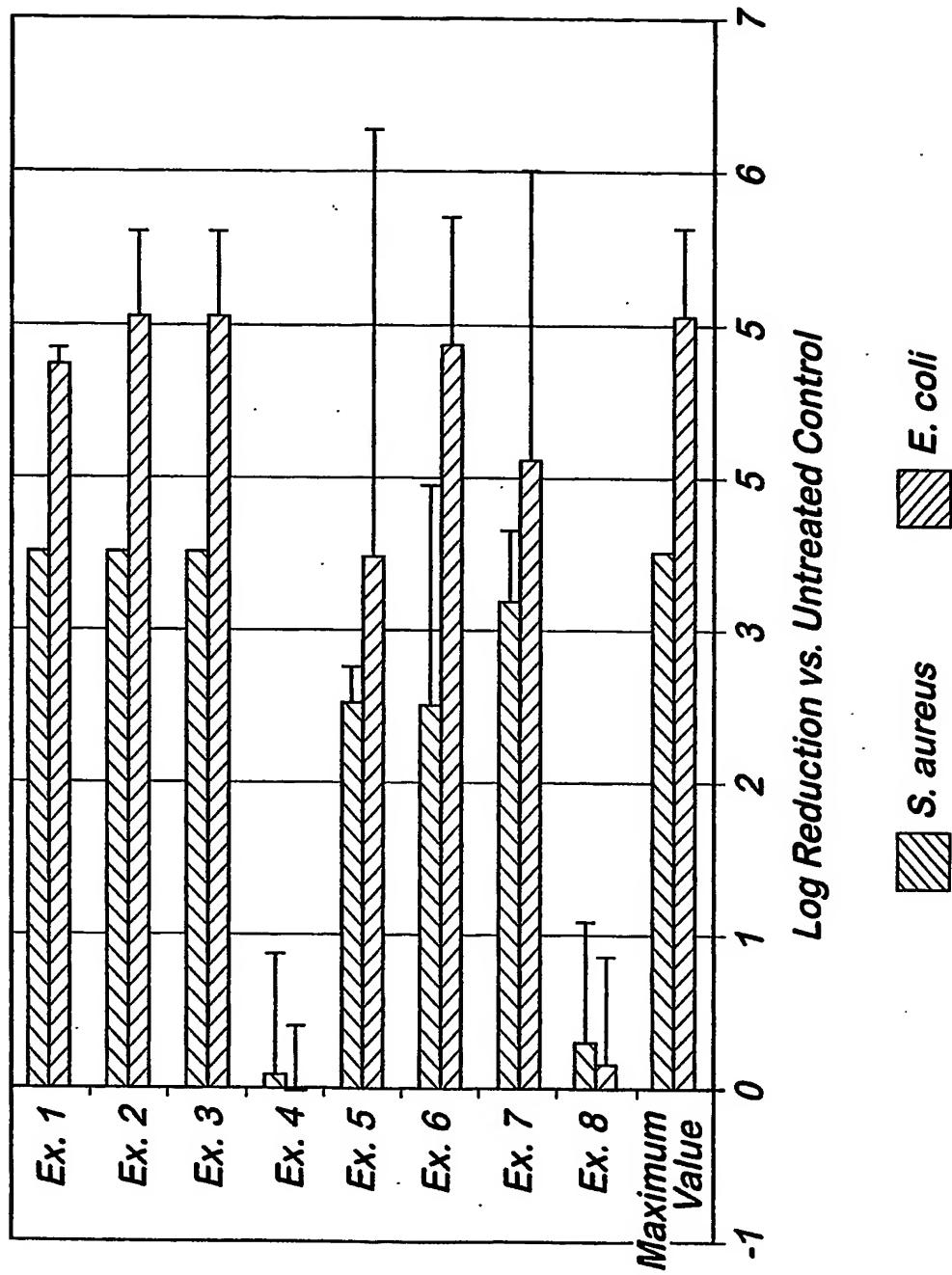
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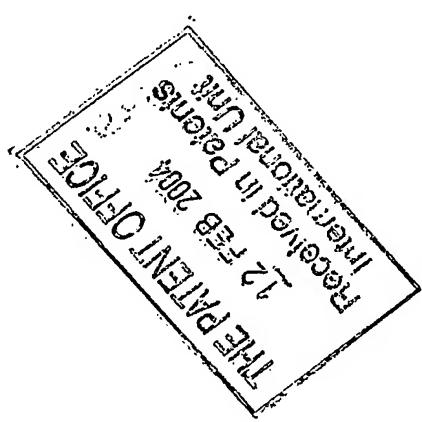
1. An anti-microbial polymeric film comprising a polymeric substrate layer and a coating comprising an anti-microbial compound in an amount of from about 0.1 to about 5.0% by weight of the coating layer, wherein said coating has a thickness of from about 0.01 to about 14.0 μm .
2. An anti-microbial film according to claim 1 wherein the anti-microbial compound has the formula $M^1_aH_bA_cM^2_2(PO_4)_3.nH_2O$ wherein:
 - 10 M^1 is at least one metal ion selected from silver, copper, zinc, tin, mercury, lead, iron, cobalt, nickel, manganese, arsenic, antimony, bismuth, barium, cadmium and chromium;
 - A is at least one ion selected from an alkali or alkaline earth metal ion;
 - M^2 is a tetravalent metal ion;
 - a and b are positive numbers and c is 0 or a positive number such that $(ka + b + mc) = 1$;
 - 15 k is the valence of metal M^1 ;
 - m is the valence of metal A; and
 - $0 \leq n \leq 6$.
3. An anti-microbial film according to claim 1 wherein the anti-microbial compound has the formula $Ag_aH_bA_cZr_2(PO_4)_3.nH_2O$ wherein:
 - 20 A is an alkali or alkaline earth metal ion;
 - a, b and c are positive numbers such that $(a + b + mc) = 1$;
 - m is the valence of metal A;
 - $0 \leq n \leq 6$.
- 25 4. An anti-microbial film according to claim 2 or 3 wherein a is in the range 0.1 to 0.5.
5. An anti-microbial film according to claim 2, 3 or 4 wherein b is at least 0.2.
- 30 6. A film according to any of claims 2 to 5 wherein the metal A is sodium and m is 1.

7. A film according to any preceding claim wherein the anti-microbial compound contains silver.
8. An anti-microbial film according to any of claims 1 to 7 wherein said coating is sufficient to provide a water vapour transmission rate in the range of 0.01 to 10g/100 inches²/day, and/or an oxygen transmission rate in the range of 0.01 to 10 cm³/100 inches²/day/atm.
9. An anti-microbial film according to any of claims 1 to 7 wherein said coating is sufficient to provide a heat-seal strength of from 100 to 2500 g/in when heat-sealed to itself.
10. An anti-microbial film according to any preceding claim wherein the haze of the film is less than 15%.
-
11. An anti-microbial film according to any preceding claim wherein the volume distributed mean particle diameter of the anti-microbial particles is in the range of 1.0 to 3.0 µm.
12. An anti-microbial film according to any preceding claim wherein the thickness of the coating layer is in the range of 70 to 130% of the volume distributed mean particle diameter of the anti-microbial particles.
13. An anti-microbial film according to any preceding claim wherein the thickness of the coating layer is less than the volume distributed mean particle diameter of the anti-microbial particles, preferably such that thickness is in the range of 70 to 99 % of the volume distributed mean particle diameter of the anti-microbial particles.
14. A film according to any preceding claim wherein said polymeric substrate is selected from polyester, polyolefin, polyamide and PVC.
15. A film according to any preceding claim wherein said polymeric substrate comprises polyester.

16. A film according to any preceding claim wherein said polymeric substrate comprises polyethylene terephthalate.
- 5 17. A film according to any preceding claim wherein the gloss is at least 70.

Fig. 1





PCT Application
PCT/GB2004/000016



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